Form PTO-1390 (Rev. 12-29-99) US DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NO: **H 4024 PCT/US**

U.S. APPLICATION NO (if known see 37 CFR 1.5): **10/049330**

| INTERNATIONAL APPLICATION NO. | INTERNATIONAL FILING DATE | PRIORITY DATE CLAIMED |
|---|---|---|
| **PCT/EP00/07496** | **August 3, 2000** | **August 11, 1999** |

TITLE OF INVENTION

**METHOD FOR PRODUCING ESTERS FROM UNSATURATED CARBOXYLIC ACIDS AND POLYHYDRIC ALCOHOLS**

APPLICANT(S) FOR DO/EO/US

**Harald Roessler, Matthias Fies, Bernhard Gutsche, Theo Stalberg**

Applicant herewith submits to the United States Designated/Elected Office (EO/DO/US) the following items and other information:

1. ■ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. □ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. □ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39 (1).
4. ■ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ■ A copy of the International Application as filed (35 U.S.C. 371(c)(2)).
   a. □ is transmitted herewith (required only if not transmitted by the International Bureau).
   b. ■ has been transmitted by the International Bureau.
   c. □ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ■ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ■ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. □ are transmitted herewith (required only if not transmitted by the International Bureau).
   b. □ have been transmitted by the International Bureau.
   c. □ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ■ have not been made and will not be made.
8. □ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ■ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). **(UNEXECUTED)**
10. □ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

**Items 11. to 16. below concern other document(s) or information included:**

11. □ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. □ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ■ A FIRST preliminary amendment
    □ A SECOND or SUBSEQUENT preliminary amendment.
14. □ A substitute specification.
15. □ A change of power of attorney and/or address letter.
16. ■ Other items or information:

Drawing (1)

**"Express Mail Post Office to Addressee" service Mailing Label Number EL541614435US .**

JC13 Rec'd PCT/PTO 11 FEB 2002

| U.S. Application No. (If known, see 37 CFR 1.5) 10/049330 | INTERNATIONAL APPLICATION NO. PCT/EP00/07496 | ATTORNEY'S DOCKET NUMBER H 4024 PCT/US |
|---|---|---|

17.■ The following fees are submitted:

| | CALCULATIONS | PTO USE ONLY |
|---|---|---|
| **BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):** Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO.....**$1,040.00** | | |
| International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO.....**$890.00** | | |
| International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37CFR 1.445(a)(2)) paid to USPTO .....**$740.00** | | |
| International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... **$710.00** | | |
| International preliminary examination fee paid to USPTO (37CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4).....**$100.00** | | |
| **ENTER APPROPRIATE BASIC FEE AMOUNT** = | $ 890 | |
| Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date 37 (CFR 1.492(e)). | $ 0 | |

| CLAIMS | NUMBER FILED | NUMBER EXTRA | RATE | | |
|---|---|---|---|---|---|
| Total Claims | 26 - 20 = | 6 | 6 X $18.00 | $ 108 | |
| Independent Claims | 2 - 3 = | 0 | 0 X $84.00 | $ 0 | |
| Multiple dependent claims (s)(if applicable) | | 0 | + $280.00 | $ 0 | |
| **TOTAL OF ABOVE CALCULATIONS** = | | | | $ 998 | |
| Reduction of ½ for filing by small entity, if applicable. A Small Entity Statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28). | | | | $ 0 | |
| **SUBTOTAL** = | | | | $ 998 | |
| Processing fee of **$130.00** for furnishing the English translation later the ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(f)). + | | | | $ 0 | |
| **TOTAL NATIONAL FEE** = | | | | $ 998 | |
| Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). $40.00 per property + | | | | $ 0 | |
| **TOTAL FEES ENCLOSED** = | | | | $ 998 | |
| | | | | Amount to be: refunded: | $---------- |
| | | | | charged: | $998.00 |

a. ☐ A check in the amount of $_____ to cover the above fees is enclosed.

b. ■ Please charge my Deposit Account No. 50-1177 in the amount of $998.00 to cover the above fees. A triplicate copy of this sheet is enclosed. Order No. 02-0068 .

c. ■ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 50-1177 . A triplicate copy of this sheet is enclosed.

**NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.**

SEND ALL CORRESPONDENCE TO: **Customer Label No. 23657**

SIGNATURE

Aaron R. Ettelman
NAME ATTORNEY FOR APPLICANT

42,516
REGISTRATION NUMBER

"Express Mail " Mailing Label Number EL541614435US .

PATENT
Docket No. H 4024 PCT/US

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

RE: PCT/EP00/07496
International Filing Date: August 3, 2000
Priority Date Claimed: August 11, 1999
Applicant: Roessler, et al.
Title: METHOD FOR PRODUCING ESTERS FROM UNSATURATED CARBOXYLIC ACIDS AND POLYHYDRIC ALCOHOLS
Applicants' Reference: H 4024 PCT/US

**PRELIMINARY AMENDMENT**

Commissioner for Patents
Box PCT
Washington, DC 20231

ATTN: DO/EO/US

Prior to the calculation of fees and examination of the above-identified national stage application pursuant to the accompanying submission under 35 U.S.C. §371, please amend the English translation of the International Application submitted herewith, without prejudice, as follows:

**In the Specification**:

Please amend the instant Specification, without prejudice, as follows:

Please delete all text above line 10 of page 1, including the heading "Prior Art", and replace the deleted matter with the following new section headings and title of the invention:

--TITLE OF THE INVENTION

Processes for Producing Esters of Unsaturated Carboxylic Acids and Polyhydric Alcohols With Limited Polymerization, and Apparatus Therefor

BACKGROUND OF THE INVENTION--

**Preliminary Amendment of U.S. National Stage for International Application PCT/EP00/07496 filed August 3, 2000**

At page 3, line 28 thereof, please delete the section heading "Description of the Invention" and insert the following new section heading:

--BRIEF SUMMARY OF THE INVENTION--

At page 4, between lines 20 and 21 thereof, please insert the following new section headings and accompanying text:

--BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING--

The drawing shows a general diagram of the apparatus according a preferred embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION--

At page 10, between lines 1 and 2, please add the following new paragraph: --What is claimed is:--.

On a separate, new page 12, please add the following new section heading and paragraph containing an Abstract of the Disclosure:

--ABSTRACT OF THE DISCLOSURE

Processes and apparatus for producing esters are described. The processes include: (a) providing a liquid reaction mixture comprising (i) an unsaturated carboxylic acid having a boiling point greater than water, (ii) a polyhydric alcohol, and (iii) a first polymerization inhibitor, in a reaction zone having an inner surface; (b) reacting the acid and the polyhydric alcohol to form an ester, such that a gas/vapor phase is formed comprising water of reaction; (c) removing at least a portion of the gas/vapor phase from the reaction zone to a dephlegmation zone having an inner surface; (d) partially condensing the portion of the gas/vapor phase in the dephlegmation zone such that a condensate is formed; and (e) returning the condensate to the reaction zone; wherein a second polymerization inhibitor is

introduced into the dephlegmation zone such that the portion of the gas/vapor phase and/or the condensate are contacted with the second polymerization inhibitor. Apparatus for carrying out the processes are also described.--

**In the Claims:**

Please add new claims 10-35, as follows:

--10. (New) A process for producing esters, said process comprising:

(a) providing a liquid reaction mixture comprising (i) an unsaturated carboxylic acid having a boiling point greater than water, (ii) a polyhydric alcohol, and (iii) a first polymerization inhibitor, in a reaction zone having an inner surface;

(b) reacting the acid and the polyhydric alcohol to form an ester, such that a gas/vapor phase is formed comprising water of reaction;

(c) removing at least a portion of the gas/vapor phase from the reaction zone to a dephlegmation zone having an inner surface;

(d) partially condensing the portion of the gas/vapor phase in the dephlegmation zone such that a condensate is formed; and

(e) returning the condensate to the reaction zone;

wherein a second polymerization inhibitor is introduced into the dephlegmation zone such that the portion of the gas/vapor phase and/or the condensate are contacted with the second polymerization inhibitor.--

--11. (New) The process according to claim 10, wherein the second polymerization inhibitor and the first polymerization inhibitor are the same.--

--12. (New) The process according to claim 10, wherein the second polymerization inhibitor introduced into the dephlegmation zone comprises a portion of the liquid reaction mixture which is removed from the reaction zone.--

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--13. (New) The process according to claim 10, wherein the inner surface of the dephlegmation zone is wetted with a mixture of the condensate and the second polymerization inhibitor.--

--14. (New) The process according to claim 10, wherein the second polymerization inhibitor is introduced into the dephlegmation zone at a temperature below the reaction temperature.--

--15. (New) The process according to claim 10, wherein a third polymerization inhibitor is introduced into the reaction zone such that a portion of the inner surface of the reaction zone which is not in contact with the reaction mixture is contacted with the third polymerization inhibitor.--

--16. (New) The process according to claim 12, wherein a third polymerization inhibitor is introduced into the reaction zone such that a portion of the inner surface of the reaction zone which is not in contact with the reaction mixture is contacted with the third polymerization inhibitor.--

--17. (New) The process according to claim 15, wherein the third polymerization inhibitor and the first polymerization inhibitor are the same.--

--18. (New) The process according to claim 15, wherein the second polymerization inhibitor, the third polymerization inhibitor and the first polymerization inhibitor are the same.--

--19. (New) The process according to claim 16, wherein the second polymerization inhibitor, the third polymerization inhibitor and the first polymerization inhibitor are the same.--

**Preliminary Amendment of U.S. National Stage for International Application PCT/EP00/07496 filed August 3, 2000**

--20. (New) The process according to claim 15, wherein the third polymerization inhibitor introduced into the reaction zone comprises a portion of the liquid reaction mixture which is removed from the reaction zone.--

--21. (New) The process according to claim 16, wherein the third polymerization inhibitor introduced into the reaction zone comprises a portion of the liquid reaction mixture which is removed from the reaction zone.--

--22. (New) The process according to claim 15, wherein the third polymerization inhibitor is introduced into the reaction zone at a temperature below the reaction temperature.--

--23. (New) The process according to claim 10, wherein air is injected into the reaction mixture during the reaction.--

--24. (New) The process according to claim 10, wherein the removal of the portion of the gas/vapor phase from the reaction zone to a dephlegmation zone is carried out under reduced pressure.--

--25. (New) The process according to claim 10, wherein the dephlegmation zone comprises a dephlegmator attached to the top of the reaction zone.--

--26. (New) The process according to claim 10, wherein the dephlegmation zone comprises a vertical tube-bundle heat exchanger.--

--27. (New) The process according to claim 10, wherein the second polymerization inhibitor is introduced into the dephlegmation zone via one or more spray nozzles.--

**Preliminary Amendment of U.S. National Stage for International Application PCT/EP00/07496 filed August 3, 2000**

--28. (New) The process according to claim 15, wherein the third polymerization inhibitor is introduced into the reaction zone via one or more spray nozzles.--

--29. (New) The process according to claim 10, wherein the unsaturated carboxylic acid comprises a component selected from the group consisting of acrylic acid, methacrylic acid and mixtures thereof.--

--30. (New) A process for producing esters, said process comprising:

(a) providing a liquid reaction mixture comprising (i) an unsaturated carboxylic acid selected from the group consisting of acrylic acid, methacrylic acid and mixtures thereof, (ii) a polyhydric alcohol, and (iii) a polymerization inhibitor, in a reaction zone having an inner surface;

(b) reacting the acid and the polyhydric alcohol to form an ester, such that a gas/vapor phase is formed comprising water of reaction;

(c) removing at least a portion of the gas/vapor phase from the reaction zone to a dephlegmation zone having an inner surface, under reduced pressure; and

(d) partially condensing the portion of the gas/vapor phase in the dephlegmation zone such that a condensate is formed; and

(e) returning the condensate to the reaction zone;

wherein a portion of the liquid reaction mixture is removed from the reaction zone and introduced into the dephlegmation zone such that the portion of the gas/vapor phase and the condensate are contacted with the portion of the liquid reaction mixture and the inner surface of the dephlegmation zone is wetted with a mixture of the condensate and the portion of the liquid reaction mixture; and wherein a second portion of the liquid reaction mixture is removed from the reaction zone and reintroduced into the reaction zone such that a portion of the inner surface of the reaction zone which is not in contact with the reaction mixture is contacted with the second portion of the liquid reaction mixture.--

**Preliminary Amendment of U.S. National Stage for International Application PCT/EP00/07496 filed August 3, 2000**

--31. (New) An apparatus for performing the process according to claim 10, said apparatus comprising the reaction zone surmounted by the dephlegmation zone, wherein the reaction zone and the dephlegmation zone are connected for fluid communication; further comprising a first pipe having a first end and a second end, the first end of the first pipe being connected for fluid communication to a lower portion of the reaction zone and the second end of the first pipe being connected to an upper portion of the dephlegmation zone, wherein at least one spray nozzle is located within the vapor pipe, the at least one spray nozzle being connected to the second end of the first pipe for fluid communication between the first pipe and the dephlegmation zone and the at least one spray nozzle being directed towards a lower portion of the dephlegmation zone; and a pump connected to the first pipe.--

--32. (New) The apparatus according to claim 31 wherein the dephlegmation zone comprises a vertical tube-bundle heat exchanger.--

--33. (New) The apparatus according to claim 31, wherein the at least one spray nozzle comprises at least two spray nozzles, at least one being directed towards the inner surface of the dephlegmation zone.--

--34. (New) The apparatus according to claim 31, further comprising cooler connected to the first pipe.--

--35. (New) The apparatus according to claim 31, further comprising a second pipe having a first end and a second end, the first end of the second pipe being connected for fluid communication to a lower portion of the reaction zone and the second end of the second pipe being connected to an upper portion of the reaction zone, wherein at least one spray nozzle is located within the reaction zone, the at least one spray nozzle being connected to the second end of the second pipe for fluid communication between the second pipe and the reaction zone and the at least one spray nozzle being directed towards a portion of the inner surface of the reaction zone which is not in contact with the reaction mixture.--

**Preliminary Amendment of U.S. National Stage for International Application PCT/EP00/07496 filed August 3, 2000**

Please cancel claims 1-9, without prejudice.

**Preliminary Amendment of U.S. National Stage for International Application PCT/EP00/07496 filed August 3, 2000**

REMARKS

Claims 10-35 are currently pending in the instant application.

The Specification has been amended to delete the original section headings and to insert the preferred section headings pursuant to 37 C.F.R. §1.77. A new Title of the Invention has been inserted. A Brief Description of the Several Views of the Drawing has also been inserted. An Abstract of the Disclosure, in accordance with the disclosure, has been added. It is submitted that the amendments to the Specification made herein introduce no new matter. All of the amendments to the Specification constitute deletions of original section headings and/or paragraphs, and insertions or additions of new section headings and/or paragraphs. Accordingly, pursuant to 37 C.F.R. §1.121(b)(1)(iii), no separate page captioned "VERSION WITH MARKINGS TO SHOW CHANGES MADE" is necessary. A separate page containing a clean copy of the Abstract of the Disclosure has been attached for the Examiner's convenience. Entry of the amendments to the Specification made herein are therefore proper and respectfully requested.

Original claims 1-9 have been canceled and replaced with new claims 10-35 solely for the purpose of improving clarity and grammar, which may suffer in translation, and not for any reason which relates to the statutory requirements for a patent. New claims 10-35 have not been added in response to any rejection, nor in anticipation of any rejection. Applicants respectfully submit that the scope of new claims 10-35 generally corresponds to the scope of original claims 1-9, and that new claims 10-35 are no narrower than original claims 1-9. Furthermore, although a moot point in view of their cancellation, Applicants respectfully submit that original claims 1-9 satisfied the requirements of 35 U.S.C. §112, as filed. New claims 10-35 are supported by the claims as originally filed and in the Specification, for example, at page 3, line 29, through page 4, line 9; at page 5, lines 4-19; and at page 6, lines 1-19;. No new matter has been introduced. All of the amendments to the Claims constitute cancellation of original claims and the addition of new claims. Accordingly, pursuant to 37 C.F.R. §1.121(c)(1)( ii), no separate page captioned "VERSION WITH MARKINGS TO SHOW CHANGES MADE" is necessary. Entry is therefore proper and respectfully requested.

**Preliminary Amendment of U.S. National Stage for International Application PCT/EP00/07496 filed August 3, 2000**

Prompt examination of the instant application in view of the amendments made herein is respectfully requested.

Respectfully submitted,

**HARALD ROESSLER,** *et al.*

February 4, 2002
(Date)

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## ABSTRACT OF THE DISCLOSURE

Processes and apparatus for producing esters are described. The processes include: (a) providing a liquid reaction mixture comprising (i) an unsaturated carboxylic acid having a boiling point greater than water, (ii) a polyhydric alcohol, and (iii) a first polymerization inhibitor, in a reaction zone having an inner surface; (b) reacting the acid and the polyhydric alcohol to form an ester, such that a gas/vapor phase is formed comprising water of reaction; (c) removing at least a portion of the gas/vapor phase from the reaction zone to a dephlegmation zone having an inner surface; (d) partially condensing the portion of the gas/vapor phase in the dephlegmation zone such that a condensate is formed; and (e) returning the condensate to the reaction zone; wherein a second polymerization inhibitor is introduced into the dephlegmation zone such that the portion of the gas/vapor phase and/or the condensate are contacted with the second polymerization inhibitor. Apparatus for carrying out the processes are also described.

# Method for Producing Esters from Unsaturated Carboxylic Acids and Polyhydric Alcohols

## Field of the Invention

This invention relates to a process for the production of esters of unsaturated carboxylic acids with a higher boiling point than water, more particularly acrylic acid or methacrylic acid, and polyhydric alcohols in a reactor, the liquid reaction mixture containing polymerization inhibitors and the water of reaction formed being at least partly removed in vaporous form.

## Prior Art

(Meth)acrylic acid esters of polyhydric alcohols, more particularly from the group of dihydric to tetrahydric aliphatic saturated alcohols and alkoxylation products thereof, are being increasingly used as highly reactive constituents in radiation-curing systems. Polyfunctional (meth)acrylic acid esters may be used, for example, as paint raw materials for electron beam hardening or as a constituent of UV-hardening printing inks or corresponding coatings, surfacing, molding or potting compounds or even in adhesives, particularly anaerobically curing adhesives. However, their production is not without problems. There is a demand above all for colorless products with a low acid value and high storage stability which also have virtually no odor of their own. Purification of the (meth)acrylic acid esters in question here by distillation is generally not possible on account of their high molecular weight and their high reactivity. Accordingly, the products should be directly obtained as colorless esterification products. Carrying out of the esterification reactions involves the presence of highly effective inhibitors which, for their part, do not initiate any unwanted secondary reactions, for example in the form of

discolorations. In addition, it can be desirable not only to protect the liquid reaction product from unwanted polymerization reactions during the esterification reaction, but also to ensure adequate inhibition of the entire reaction space including both the inner gas space and the wall surfaces which come into contact with the inner gas space. This counteracts the danger of unwanted polymer formation, for example on unprotected walls, the washing off of such polymers into the reaction product leading to an unwanted increase in the viscosity of the end product or to unwanted insoluble particles.

However, the invention is not confined to the production of (meth)acrylic acid esters, but instead relates to any esters of unsaturated carboxylic acids with a higher boiling point than water and polyhydric alcohols.

The above-described process is known, for example, from **DE 3843843 A1**. The reaction space is purged with an oxygen-containing gas stream and that part of the inner reaction space which is filled with the gas phase is charged with fine droplets of liquid which contain the polymerization inhibitor. In this way, not only is the reactive liquid phase effectively stabilized by polymerization inhibitors, the entire inner reaction space is protected against unwanted polymerization reactions. The same inhibitor is used both for protecting the reactive liquid phase and for protecting the gas- or vapor-filled inner space and the solid surfaces (inner walls, stirrer components, etc.) arranged therein. In another process of the type mentioned at the beginning, the water of condensation formed during the reaction is removed from the gas phase of the reaction space. Finally, **DE 3843930 A1** describes the polymerization inhibitors preferably used in the process mentioned at the beginning.

In the acid-catalyzed batch or semibatch esterification process, an inhibitor system which acts chemically in the liquid reaction mixture and which consists, for example, of a hydroquinone derivative in combination

with atmospheric oxygen is used to prevent polymerization both of the unsaturated carboxylic acid used and of the unsaturated polyol ester formed. During the esterification, the water of reaction formed is removed from the reaction mixture by distillation under reduced pressure to obtain high conversion levels. With volatile unsaturated carboxylic acids, such as acrylic and methacrylic acid, a water/carboxylic acid mixture with a composition corresponding to the phase equilibrium is removed from the circuit. This known process has two major disadvantages when used for the esterification of volatile unsaturated carboxylic acids:

- First, the removal of water/carboxylic acid from the circuit inevitably leads to a large stoichiometric excess of carboxylic acid, based on the polyol used, which can amount to between 40 and 50% in the case of tri- and tetrahydric polyols.
- Second, the hydroquinone/air system - which only has an inhibiting effect in the liquid reaction mixture - is attended by the danger that the noninhibited unsaturated carboxylic acid present in the gas phase during the removal of water from the circuit polymerizes during the condensation, leading to serious problems in the process.

Accordingly, the problem addressed by the present invention was significantly to reduce the excess of carboxylic acid in the process mentioned at the beginning and to prevent the polymerization of carboxylic acid or ester in the liquid or gas phase. In addition, the reaction time would be shortened and the level of organic pollutants in the wastewater would be reduced.

**Description of the Invention**

Accordingly, the present invention relates to a process for the production of esters of unsaturated carboxylic acids with a higher boiling

point than water, more particularly acrylic acid or methacrylic acid, and polyhydric alcohols in a reactor, the liquid reaction mixture containing polymerization inhibitors and the water of reaction formed being at least partly removed in vaporous form, characterized in that part of the gas/vapour phase of the reaction mixture is removed from the reactor and is partly condensed in a dephlegmator, a liquid containing the polymerization inhibitor is introduced into the ascending gas/vapor mixture and the descending condensate from the head of the dephlegmator and the entire outflowing mixture is returned to the reactor.

In the condensate which is enriched with carboxylic acid, polymerization is prevented by addition of the inhibitor so that the condensate can readily be returned to the reaction mixture. This recycling enables the carboxylic acid excess required for the reaction to be reduced from 20-40% in the known process to 5-10. The partial condensation of the unsaturated carboxylic acid leads to a vapor phase distinctly enriched with water and hence to faster distillation and a shorter reaction time. After removal from the circuit, the water-enriched vapor phase is condensed, the condensate being disposed of as wastewater. In contrast to the prior art, this wastewater contains a far lower percentage of unsaturated carboxylic acids and, accordingly, has a far lower level of organic pollutants.

According to the invention, an external inhibitor solution may be added to the condensate enriched with carboxylic acid. In one particularly advantageous embodiment, however, part of the liquid reaction mixture is branched off for this purpose and is added to the ascending gas/vapor mixture and to the descending condensate. Part of the liquid reaction mixture is thus circulated.

The above-mentioned cooling of the gas/vapor phase of the reaction mixture removed from the circuit can be effected by spraying a comparatively cold liquid containing the inhibitor - more particularly the reaction mixture - into the vapor pipe. It has been found to be possible in

this way, i.e. without using a dephlegmator, both to separate carboxylic acid and water and to prevent polymerization of the condensed carboxylic acid.

In a preferred embodiment, however, the gas/vapor mixture removed from the reaction mixture can be partly condensed in a dephlegmator, a liquid phase enriched with carboxylic acid running off and a water-rich vapor phase leaving the dephlegmator and wetting its inner walls with the liquid containing the polymerization inhibitor. Particularly effective separation of water and carboxylic acid is achieved through the use of the dephlegmator. In one particular embodiment, a vertical tube-bundle heat exchanger of stainless steel is used as the dephlegmator. By spraying the inner walls of the dephlegmator, inhibition is achieved immediately after condensation of the carboxylic acid.

It has also been found that the separation of carboxylic acid and water is further improved if the liquid containing the polymerization inhibitor has a temperature below or at most up to the reaction temperature. Accordingly, after part of the reaction mixture has been branched off, this part is preferably cooled before it is sprayed onto the inner walls of the dephlegmator.

In order to ensure that the condensed mixture enriched with unsaturated carboxylic acid which flows back into the reactor does not under any circumstances polymerize on the inside of the reactor cover or on internals in the upper interior of the reactor, for example on parts of the stirrer, the condensate is returned to the reactor from above and a liquid containing the polymerization inhibitor, more particularly a part branched off from the liquid reaction mixture, is fed to and more particularly sprayed onto the inner walls and internals in the upper part of the reactor, more particularly the inner wall of the reactor cover. In this way, the tendency of the condensate to polymerize on the parts mentioned is effectively prevented.

The present invention also relates to an installation for carrying out the described process comprising a reactor surmounted by a vapor pipe for removing water from the reaction mixture.

In this case, the above-stated problem addressed by the invention is solved by a first pipe extending from the lower part of the reactor to the vapor pipe, first spray nozzles arranged within the vapor pipe at the outlet of the first pipe, the spray nozzles being directed in particular oppositely to the ascending vapors, and a pump in the first pipe.

In a particularly preferred embodiment, the vapor pipe is in the form of a dephlegmator surmounting the reactor and the first spray nozzles are directed onto the inner walls of the dephlegmator.

In addition, in order further to improve the separation of water and carboxylic acid in the condensate, a cooler in the first pipe is of advantage.

In order to prevent polymerizations in the upper inner part of the reactor, a second pipe - either extending from the lower part of the reactor or branched off from the first pipe - is provided and second spray nozzles are arranged at the outlet of the second pipe and are directed onto the inner walls and internals in the upper part of the reactor, more particularly onto the inner wall of the reactor cover.

One example of embodiment of the installation according to the invention is described in detail in the following with reference to the accompanying drawing (Fig. 1) which schematically illustrates the plant.

The liquid reaction mixture 1 in the heated reactor 2 is mixed by a stirrer 4 driven by a motor 3. The reaction mixture 1 contains the polymerization inhibitor, the unsaturated carboxylic acid, the polyhydric alcohol and the secondary reaction product, water, and the reaction product, the ester. Air is injected into the reaction mixture 1 from below through a pipe 5.

The vapor phase above the liquid reaction mixture 1 is removed under reduced pressure through a dephlegmator 6 fitted onto the reactor 2.

The dephlegmator is a vertical tube-bundle heat exchanger of which the inner walls are indicated by chain lines. After removal of most of the carboxylic acid, the water-enriched vapor phase is removed upwards and liquefied in a condenser (not shown). The water containing only a relatively small amount of carboxylic acids is disposed of as wastewater. The dephlegmator 6 is cooled with water through pipes 16.

From the bottom of the reactor 2, a first pipe 7 leads via a filter 8, which retains polymerized fractions, a pump 9 and a valve 10 to first spray nozzles 11 in the upper part of the dephlegmator 6. The first spray nozzles 11 are directed downwards onto the inner walls of the dephlegmator 6.

Branching off from the first pipe 7 is a second pipe 12 through which the reaction mixture 1 passes via a valve 13 to second spray nozzles 14 which are arranged in the upper part of the reactor 2 above the liquid surface and which are directed upwards onto the inner wall of the reactor cover 15.

The installation operates as follows:

Water/carboxylic acid vapors ascend from the liquid heated reaction mixture into the dephlegmator 6. At the same time, the inhibited liquid reaction mixture flows in countercurrent down the inner walls of the dephlegmator 6 and - similarly to a rectifying column operated under reflux - intensifies the separation of carboxylic acid and water. In addition, the condensed unsaturated carboxylic acids are prevented from polymerizing on the walls of the dephlegmator.

In the upper part of the inner reactor space, the inhibited reaction mixture is sprayed by the second spray nozzles 14 arranged on a nozzle ring onto the inner wall of the reactor cover 15 and onto the noninhibited carboxylic acid flowing down the reactor cover from the dephlegmator 6. Polymerization in the cover region of the reactor is prevented in this way.

A vertical tube-bundle reactor with a liquid inlet at its head via the first spray nozzles 11 is used as the dephlegmator 6. The ratio of tube

diameter to tube length is at least 0.03:1. The heat exchanger has an exchange area of at least 10 $m^2$ per $m^3$ reactor volume.

**List of Reference Numerals**

| | |
|---|---|
| 1 | reaction mixture |
| 2 | reactor |
| 3 | motor |
| 4 | stirrer |
| 5 | pipe |
| 6 | dephlegmator |
| 7 | first pipe |
| 8 | filter |
| 9 | pump |
| 10 | valve |
| 11 | first spray nozzles |
| 12 | second pipe |
| 13 | valve |
| 14 | second spray nozzles |
| 15 | reactor cover |
| 16 | pipe |

**CLAIMS**

1. A process for the production of esters of unsaturated carboxylic acids with a higher boiling point than water, more particularly acrylic acid or methacrylic acid, and polyhydric alcohols in a reactor (2), the liquid reaction mixture (1) containing polymerization inhibitors and the water of reaction formed being at least partly removed in vaporous form, characterized in that part of the gas/vapour phase of the reaction mixture (1) is removed from the reactor (2) and is partly condensed in a dephlegmator (6), a liquid containing the polymerization inhibitor is introduced into the ascending gas/vapor mixture and the descending condensate from the head of the dephlegmator (6) and the entire outflowing mixture is returned to the reactor (2).

2. A process as claimed in claim 1, characterized in that part of the liquid reaction mixture (1) is branched off and introduced into the ascending gas/vapor mixture and the descending condensate.

3. A process as claimed in claims 1 and/or 2, characterized in that the gas/vapor phase removed from the reaction mixture (1) is partly condensed in a dephlegmator (6), a liquid phase enriched with carboxylic acid running off and a water-rich vapor phase leaving the dephlegmator (6) and wetting its inner walls with the liquid containing the polymerization inhibitor.

4. A process as claimed in at least one of claims 1 to 3, characterized in that the liquid containing the polymerization inhibitor has a temperature below or at most up to the reaction temperature.

5. A process as claimed in at least one of claims 1 to 4, characterized in that the condensate is returned to the reactor from above and a liquid containing the polymerization inhibitor, more particularly a part branched off from the liquid reaction mixture (1), is fed to and more particularly sprayed onto the inner walls and internals in the upper part of the reactor (2), more particularly the inner wall of the reactor cover (15).

6. An installation for carrying out the process claimed in at least one of

claims 1 to 5 comprising a reactor (2) surmounted by a vapor pipe for removing water from the reaction mixture (1), characterized in that it comprises a first pipe (7) extending from the lower part of the reactor (2) to the vapor pipe, first spray nozzles (11) arranged within the vapor pipe at the outlet of the first pipe (7), the spray nozzles (11) being directed in particular oppositely to the ascending vapors, and a pump (9) in the first pipe (7).

7. An installation as claimed in claim 6, characterized in that the vapor pipe is in the form of a dephlegmator (6) surmounting the reactor (2) and the first spray nozzles (11) are directed onto the inner walls of the dephlegmator (6).

8. An installation as claimed in claims 6 and/or 7, characterized in that it comprises a cooler in the first pipe (7).

9. An installation as claimed in at least one of claims 6 to 8, characterized in that a second pipe (12) - either extending from the lower part of the reactor (2) or branched off from the first pipe (7) - is provided and second spray nozzles (14) are arranged at the outlet of the second pipe (12) and are directed onto the inner walls and internals in the upper part of the reactor, more particularly onto the inner wall of the reactor cover (15).

(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG

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(81) Bestimmungsstaaten *(national)*: KR, US.

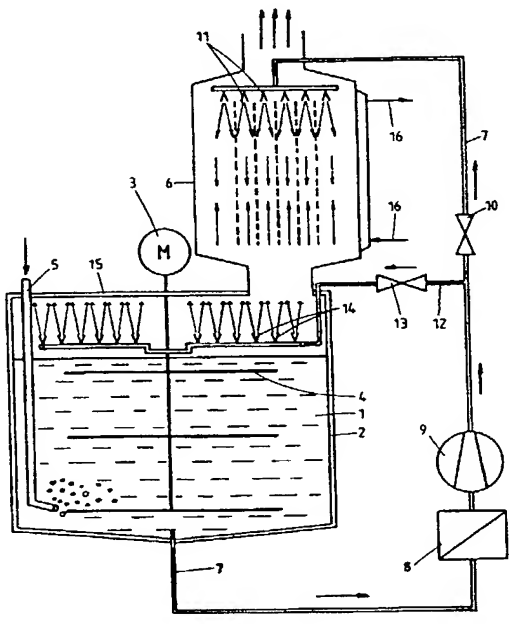
(84) Bestimmungsstaaten *(regional)*: europäisches Patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

**Veröffentlicht:**
— *Mit internationalem Recherchenbericht.*
— *Vor Ablauf der für Änderungen der Ansprüche geltenden Frist; Veröffentlichung wird wiederholt, falls Änderungen eintreffen.*

*Zur Erklärung der Zweibuchstaben-Codes, und der anderen Abkürzungen wird auf die Erklärungen ("Guidance Notes on Codes and Abbreviations") am Anfang jeder regularen Ausgabe der PCT-Gazette verwiesen.*

(54) Title: METHOD FOR PRODUCING ESTERS FROM UNSATURATED CARBOXYLIC ACIDS AND POLYHYDRIC ALCOHOLS

(54) Bezeichnung: VERFAHREN ZUM HERSTELLEN VON ESTERN AUS UNGESÄTTIGTEN CARBONSÄUREN UND MEHRWERTIGEN ALKOHOLEN




(57) **Abstract:** The invention relates to a method for producing esters from unsaturated carboxylic acids with a higher boiling point than water, especially acrylic acid or methacrylic acid; and polyhydric alcohols in a reactor (2). The liquid reaction mixture (1) contains polymerisation inhibitors and the reaction water that is produced is at least partially separated in a vapour state. The method is characterised in that part of the gas-vapour phase of the reaction mixture (1) is removed from the reactor (2), said part of the gas-vapour phase is partially condensed in a dephlegmator (6), a liquid containing the polymerisation inhibitor is added to the rising gas/vapour mixture and to the off-running condensate from the head of the dephlegmator (6) and the complete off-running mixture is returned to the reactor (2).

(57) **Zusammenfassung:** Vorgeschlagen wird ein Verfahren zum Herstellen von Estern aus ungesättigten Carbonsäuren mit einem höheren Siederpunkt als Wasser, insbesondere Acrylsäure oder Methacrylsäure, und mehrwertigen Alkoholen in einem Reaktor (2), wobei das flüssige Reaktionsgemisch (1) Polymerisationsinhibitoren enthält und wobei man das entstehende Reaktionswasser im dampfförmigen Zustand zumindest teilweise abtrennt, welches sich dadurch auszeichnet, daß man einen Teil der Gas/Dampfphase des Reaktionsgemisches (1) aus dem Reaktor (2) entfernt, diese in einem Dephlegmator (6) partiell kondensiert, dem aufsteigenden Gas-/Dampfgemisch sowie dem ablaufenden Kondensat vom Kopf des Dephlegmators (6) her eine den Polymerisationsinhibitor enthaltende Flüssigkeit zuführt und das gesamte ablaufende Gemisch wieder in den Reaktor (2) zurückführt.

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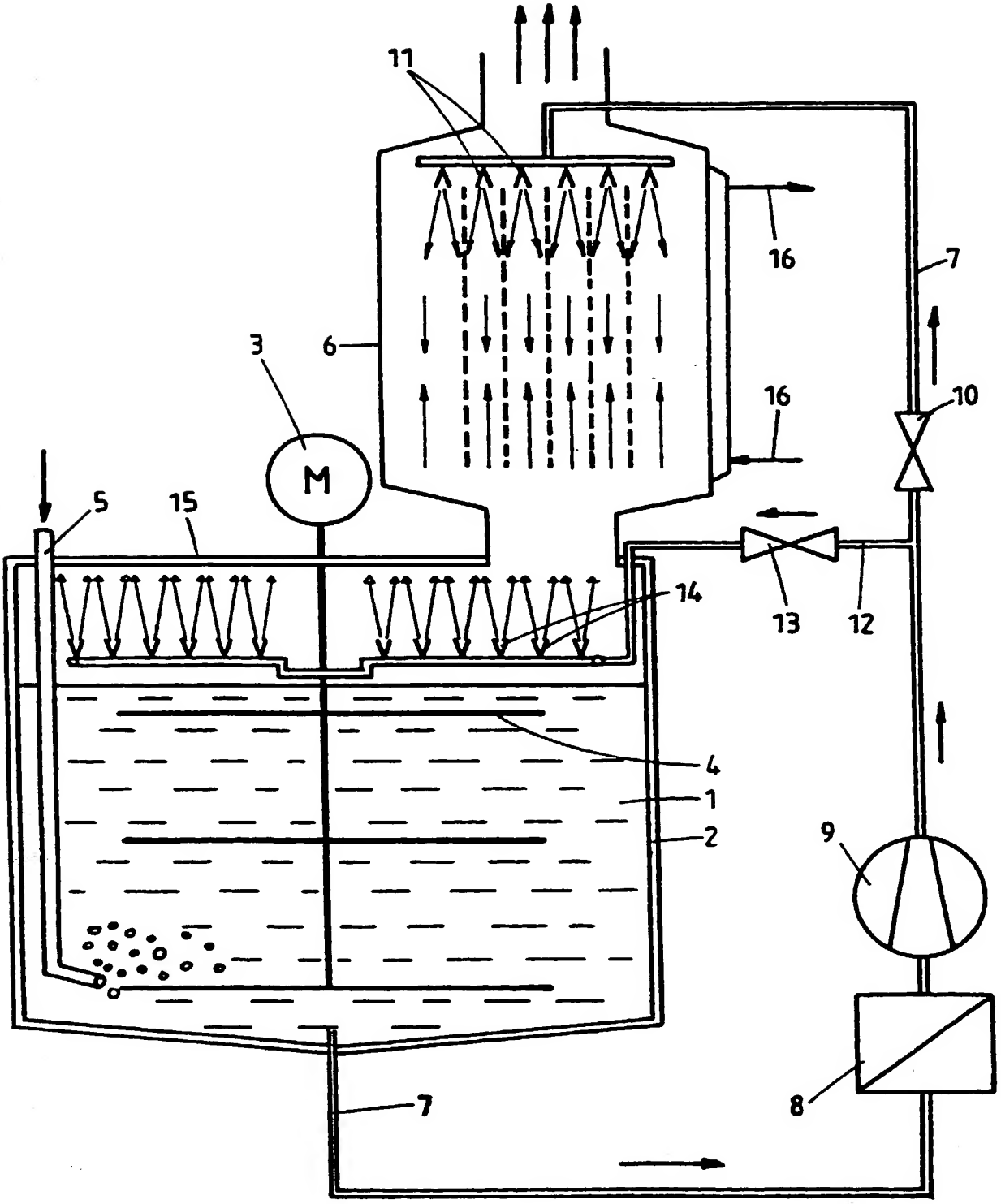
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# DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION

☐ Declaration Submitted with Initial Filing OR ☒ Declaration Submitted after Initial Filing

| | |
|---|---|
| Attorney Docket Number | H 4024 PCT/US |
| First Named Inventor | ROESSLER, Harald |
| *COMPLETE IF KNOWN* | |
| Application Number | 10/049,330 |
| Filing Date | 06/14/2002 |
| Group Art Unit | |
| Examiner Name | |

As a below named inventor, I hereby declare that:
My residence, post office address, and citizenship are as stated below next to my name.
I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

METHOD FOR PRODUCING ESTERS FROM UNSATURATED CARBOXYLIC ACIDS AND POLYHYDRIC ALCOHOLS

*(Title of the Invention)*

the specification of which

☐ is attached hereto

OR

☒ was filed on (MM/DD/YYYY) 08/03/2000 as United States Application Number or PCT International Application Number PCT/EP00/07496 and was amended on (MM/DD/YYYY) _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37 Code of Federal Regulations, § 1.56

I hereby claim foreign priority benefits under Title 35, United States Code §119(a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT International application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or of any PCT International application having a filing date before that of the application on which priority is claimed

| Prior Foreign Application Number(s) | Country | Foreign Filing Date (MM/DD/YYYY | Priority Not Claimed | Certified Copy Attached? YES | Certified Copy Attached? NO |
|---|---|---|---|---|---|
| 199 37 911.4 | DE | 08/11/1999 | ☐ | ☐ | ☒ |

☐ Additional foreign application numbers are listed on a supplemental priority sheet attached hereto:

I hereby claim the benefit under Title 35, United States Code §119(e) of any United States provisional application(s) listed below.

| Application Number(s) | Filing Date (MM/DD/YYYY) |
|---|---|
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☐ Additional provisional application numbers are listed on a supplemental priority sheet attached hereto.

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# DECLARATION



I hereby claim the benefit under Title 35, United States Code §120 of any United States application(s), or §365(c) of any PCT international application designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT international application in the manner provided by the first paragraph of Title 35, United States Code §112.1 acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

| U.S. Parent Application Number | PCT Parent Number | Parent Filing Date (MM/DD/YYYY) | Parent Patent Number *(if applicable)* |
|---|---|---|---|
| | PCT/EP00/07496 | 08/03/2000 | |

☐ Additional U.S. or PCT international application numbers are listed on a supplemental priority sheet attached hereto.

As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

☐ Firm Name OR Customer Number or label

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Name of Sole or First Inventor: ☐ A petition has been filed for this unsigned

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☒ Additional inventors are being named on supplemental sheet(s) attached hereto

Type a plus sign (+) inside this box [ ]

# DECLARATION

**ADDITIONAL INVENTOR(S) Supplemental Sheet**

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**Name of Additional Joint Inventor, if any:** ☐ A petition has been filed for this unsigned inventor

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|---|---|---|---|---|---|---|---|
| Given Name | | Middle Initial | | Family Name | | Suffix e.g. Jr. | |
| Inventor's Signature | | | | | | Date | |
| Residence: City | | State | | Country | | Citizenship | |
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